Eur. Phys. J. D **34**, 59–61 (2005)
DOI: 10.1140/epjd/e2005-00119-4

**THE EUROPEAN
PHYSICAL JOURNAL D**

Structural and electronic properties of C_6 cluster

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Received 6 September 2004

Abstract. First-principles total-energy calculations of structural properties of the carbon cluster C_6 have been made using the full-potential augmented plane-waves plus local orbital (APW+LO) method with the generalized gradient approximation (GGA). Initiated from a hexagonal configuration, we performed geometry optimization with damped Newton dynamics. The computed ground state atomic configuration for C_6 belongs to a monocyclic D_{3h} structure. The average bond length is 1.52 a.u. and the bond angle is 90.2°, respectively, which are in agreement with the reported results.

PACS. 31.15.Ar Ab initio calculations – 31.15.Qg Molecule dynamics and other numerical method – 36.40.-c Atomic and molecular clusters

Owing to their unusual electronic and structural properties, small clusters have received considerable attention recently [1,2]. Intense interest in the small carbon clusters C_{2-5} is one of the good examples of the flurry of studies [3–5]. A remarkable characteristic of clusters is the changes in their physical and chemical properties with the size. In early studies, most of the larger carbon clusters were believed to be linear species. However, recent work has pointed out that the configurations of small carbon clusters may be cyclic [6]. So it is a fundamental problem to understand the evolution of configurations and properties of carbon clusters by increasing the size from an atom to a bulk crystal. For small carbon clusters, some of the changes in properties with size is striking. These changes are strongly related with their atomic structures, which differ substantially from that of the bulk crystal. Clearly, the role of the surface induced properties become increasingly important with decreasing size of clusters. However, most of structural calculations have been performed either using semi-empirical techniques or have been restricted to small basis set Hartree-Fork studies [7]. For bare carbon clusters, unsaturated carbon bonds can exit on the surface. These dangling carbon bonds can result in unusual structures and properties. This phenomenon can be seen on the free surface of a bulk crystal. The impressing example is the (7 × 7) reconstruction for the (111) cleavage plane of the Si crystal [8]. In small carbon clusters, where almost all the carbon atoms reside on the surface, this phenomenon is reflected in structures that deviate substantially from that of their crystalline material.

While the properties of clusters offer new and novel states of matter, the synthesis and characterization of small clusters encounter numerous difficulties. Since clusters of atoms are, by definition, only stable in isolation, experimentalists face the challenge of maintaining an isolated system while probing its properties. Typical experimental techniques include cluster deposition on the inert substrate [9], and the use of cluster beam for photoemission measurements [10]. Theoretical studies of clusters are also challenging due to the many degrees of freedom, and the lack of good structural information. Structural determinations are not easy considering that the atomic arrangements and coordination can differ considerably from that of the equivalent crystal. Some of the different configurations of a moderately sized cluster have almost the same local minima in the potential-energy surface, which further complicated this problem. For clusters with more than ten or so atoms, it is impossible to make a inventory and decide by direct calculations which geometry is lowest in energy. At present there are few reliable methods for predicting the structure of a given cluster. In this paper, we will present first-principles calculations for the ground state configuration of carbon cluster C_6.

The key problem in determining the structure of a cluster is to develop a method which can accurately account for energies and interatomic forces. One approach applies empirical interatomic potentials, which are usually obtained by fitting to the known crystalline forms. The method is not necessarily a good approximation, for it requires a careful construction and accurate knowledge of the chemical bonding. Since clusters often have bonding configurations that differ substantially from the crystalline phase, the database used to fit empirical potentials may often prove inadequate when determining the parameters.

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Another important method is the ab initio pseudopotentials (PP). The physical idea behind the pseudopotentials is to replace the true atomic potential by an effective potential that accurately mimics the effect of the chemically inert core on the valent states, explicitly treated in the calculation. In this approach, one has to choose which states are to be represented by pseudo wavefunctions and an atomic reference configuration on which to generate the all electron potential and wave functions. Then, for each angular momentum, one has to choose a cutoff radius, beyond which the pseudo wavefunction is set equal to the true wave function. It is necessary to test the accuracy of the generated pseudopotentials with great caution. The pseudopotential method has been applied to a variety of clusters, resulting in good agreement with experimental results [11].

In the present paper, we focus on the all-electron full-potential augmented plane-wave plus local orbital method (APW+LO) within density functional theory. In this method, space is divided into two regions and different basis expansions of wavefunctions are used in these regions: radial solutions of Schrödinger's equation inside non-overlapping atom centered spheres and planewaves in the remaining interstitial region, and potentials are in dual presentations without shape approximation [12]. As one of the all-electron methods, APW+LO calculation is an expensive computational problem in contrast to pseudopotential method, but it is among the most accurate methods and can naturally account for the charge transfers for performing electronic structure calculations for crystals. This method can also be extended to simulate the properties of surfaces and clusters by supercell approaches. This is the reason why we have decided to use the APW+LO method to determine the ground configuration of C_6 cluster.

While APW+LO method provide a accurate accounting for computing structural energies and interatomic forces, it is still unresolved that how to select energetically favorable structures. For relatively small clusters, one can make an inventory of all possible structures and investigate one by one. Thus the true ground state can be obtained. Unfortunately, as the cluster size exceeds a few atoms, the number of the competing structures becomes quite large. The computation cost becomes unacceptable and the method hardly works in practice. As far as C_6 concerned, we optimize the cluster structure with damped Newton dynamics. In this scheme, the atomic positions evolve according to

$$R_m^{t+1} = R_m^t + \eta_m (R_m^t - R_m^{t-1}) + \delta_m F_m^t \qquad (1)$$

where R_m^t and F_m^t are the coordinate and force at time step t, δ determines the speed of atomic motion and η is the friction parameter for damped Newton scheme.

Our calculations for C_6 cluster are carried out using the WIEN2k implementation of the APW+LO method [13]. The generalized gradient approximation (GGA) [14] is adopted for the exchange-correlation potential. The C_6 cluster is modelled by a triclinic supercell, which is the distortion of the hexagonal cell with the basis vectors about $12.5a_0$ (a_0 is the Bohr radius) long, to realize the full relaxation of the six carbon atomic positions. The supercell is big enough to simulate the bare carbon cluster C_6 after our test calculations. The muffin-tin sphere radii are chosen to be $1.2a_0$ for all six carbon atoms. The $2s$, $2p$ electrons are treated as valence electrons. Converged results are obtained with $R_{MT}K_{max}$ set to be 6.0. A set of $3 \times 3 \times 3$ special $\mathbf{k}$ points is used for integrations over the Brillouin zone with the modified tetrahedron method [13] after convergence test. Six carbon atoms lie in the center of the supercell, arranging into a hexagon as an initial configuration. Then all the carbon atoms move to the equilibrium positions according to the damped Newton dynamics scheme. In our calculations, the friction coefficient is chosen to be 0.9 and the minima on the potential surface is obtained until the calculated atomic force for each carbon atom is smaller than 1 mRy/a_0. Thus the ground configuration of the C_6 cluster is obtained.

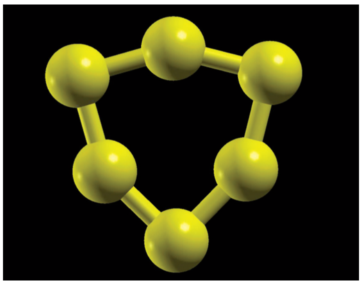

Fig. 1. Ground state structure of the C_6 cluster.

Table 1. The calculated structural parameters of C_6 cluster using different method.

method	bond length (a_0)	bond angle (degree)
APW+LO	2.52	90.2
PP[15]	2.50	91.5
B3LYP[7]	2.52	91.12
HF/6-31G^*[16]	2.49	90.4
BLYP[17]	2.51	92.9

The calculated lowest energy structure for C_6 is shown in Figure 1. The geometry for the C_6 cluster belongs to the monocyclic D_{3h} structure, which do not resembles the Si_6 with a bipyramid cone structure but is similar to the Cd_3S_3 semiconductor cluster. The bipyramid cone configuration, as another possible initial geometry of C_6 cluster, has also been tested. But the three-dimensional structure has much higher energy than the planar configuration. Thus the true atomic configuration of C_6 has been obtained. The average bond length is $1.52a_0$, and the sharp bond angle between the nearest carbon bonds is 90.2°. While experimental data are lacking for the bare clusters, we can only compare the structure with reported theoretical results. As seen in Table 1, our calculations are reliable and can be used for further studies on the properties of C_6 clusters.

We now come to the optical absorption of C_6 cluster. Although the traditional density-functional (DFT) formalism [18,19] is a powerful tool in predicting the ground-state properties of many-electron systems, the description

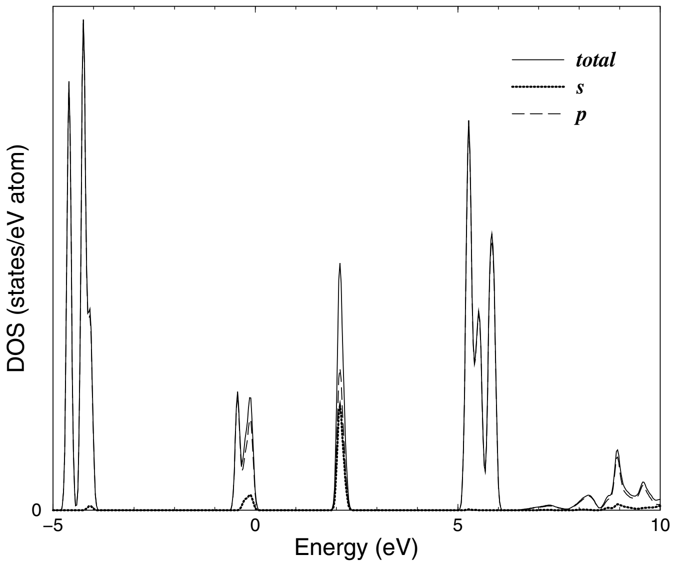

Fig. 2. Density of the states (DOS) of one carbon atom in C_6 cluster. The solid line is the total DOS, the dotted line and the long-dashed line are the DOS of the s and p orbitals, respectively. The zero-point of the energy is chosen at the top of the highest occupied orbital.

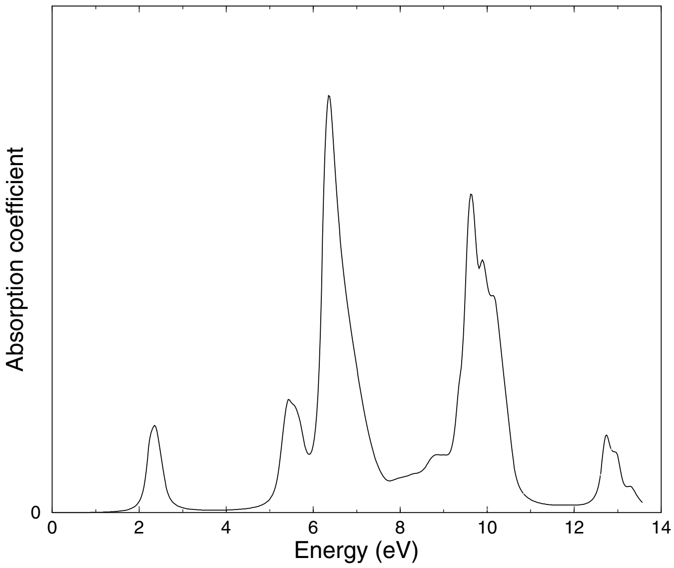

Fig. 3. The calculated optical absorption spectra for the C_6 cluster with a monocyclic D_{3h} symmetry structure.

of excited-state properties within DFT, is notoriously difficult. Beyond the limitation, the time-dependent local-density approximation (TDLDA) has been widely applied to the collective electronic excitations of atomic clusters. Even so, we can obtain some qualitative results in the linear optical response of C_6 cluster. In Figure 2, the highest occupied states are mainly p electrons, while the lowest unoccupied orbitals are the hybridization of the $s-p$ electrons. It is noted from Figure 3 that four intense absorption peaks near 2.4 eV, 6.4 eV, 9.7 eV and 12.8 eV characterize the calculated optical absorption spectra, respectively. Combined with Figure 2, it is clear that the first absorption peak responds to the energy-gap transitions and the remaining three peaks can be distinguished in the similar way.

In summary, the ground state structure for C_6 clusters is calculated using the APW+LO method coupled with the damped Newton dynamics. The obtained structural parameters are in good agreement with the reported results. As a further study, the absorption spectra for the C_6 cluster reveal four peaks in response to different electronic transitions on the basis of the independent-electron approximation.

This work was supported by the National Science Fund for Distinguished Young Scholars under Grant No. 10025416, the National Natural Science Foundation of China under Grant No. 19974075 and 10204024, the National High-Tech ICF Committee in China, and the China Research Association of Atomic and Molecular Data.

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